

A Study on the Pozzolan Properties of Pennisetum Purpureum Ash

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Abstract

Pozzolan properties of Pennisetum purpureum grass ash were tested on Portland cement. Results show that the ash can be blended with cements without compromising binding strength of the cement. It was found that Portland cement could be blended with Pennisetum purpureum up to a ratio of 3:2 compromising compressive strength of mortar. Mortar with lower cement replacement took longer to set as evidenced by lower compressive strength within the 28-day aging time. Mortar with higher cement replacement had lower water absorption capacity, an indication that the test pozzolan was of smaller particulate size. XRF analysis and the FTIR spectrum showed that the ash has a higher content of silica. The XRD pattern of the ash showed that the ash was predominantly amorphous. SEM images showed that the ash produced at 600oC had residual carbon material.

Introduction

Reports in the literature suggest that global cement manufacturing contributes about 5 % anthropogenic carbon dioxide emissions [1, 2]. Carbon dioxide is one of the greenhouse gases responsible for the increase in global warming. The debate on reduction of green gases has been going on for more than 20 years and has been subject of discussion at major international conferences, e.g. The Kyoto Protocol. To mitigate against release of huge volumes of carbon dioxide in cement manufacture, a number of pozzolans are being developed as substitutes in the cement manufacture. Pozzolans are inexpensive, naturally occurring and manmade siliceous materials that can be used as cement substitutes in mortar or concrete mixtures. They participate in a cementitious reaction with calcium hydroxide (lime) and other alkalis.

The major sources of pozzolans suitable for various applications include, ashlike deposits from volcanic activity, fired and crashed clay, furnace slag from industrial processes and organic ash from burning coal. A number of researchers have reported on potential pozzolan materials and these include rice husk ash [3, 4], zeolites [5], metakaolin [6], silica fumes [7], coal fly ash [8] and slag. Use of such material in cement manufacture contribute towards reduction of energy consumption and release of carbon dioxide.

We report a potential application of *Pennisetum purpureum* ash, better known as elephant grass ash as a pozzolan in cement production. The grass grows to a height of upto 2 metres and is found in many parts of Africa inclusive of Zimbabwe (Figure 1). It is mostly used as thatching grass, although most of it is burnt out during land clearance and cut to improve visibility along roadsides.



Figure 1: Picture of *Pennisetum purpureum*

Experimental

Elephant grass was harvested from the Scientific and Industrial Research and Development Centre farm, in Harare. The grass was sun dried and pulverized in a laboratory mill. The pulverized sample was acid leached in a 2 M HCl solution. The acid leached sample

initially burnt out to remove most of the carbonaceous material before being ignited in a muffle furnace at 650 °C for one hour to get rid of any residual carbon material. The resultant white ash sample was characterized as explained below.

A Thermo Fisher Scientific Nicolet iS5 MIR FTIR spectrophotometer equipped with an ATR iD7 accessory and OMNIC software was used to record spectra of ash samples. A GBC Quantima 120 ICP-AES was used in the determination of cation exchange capacity as described below. A Pananalytical Laboratory Axios 172 Series wavelength dispersive XRF spectrophotometer was used to determine the elemental composition of the *Pennisetum purpureum* ash. A Joel JSM 6510 microscope was used to record SEM images of ash samples. Ash samples were prepared on sample powder holder.

For the determination of pozzolanic properties, Portland cement samples were first blended with *Pennisetum purpureum* ash in the ratios of 4:1, 18:7, and 3:2 as summarized in Table 1. Selected pozzolanic properties of the ash samples which included cation exchange capacity, compressive strength, strength activity index, electrical conductivity, lime absorption and water absorption were determined as described below.

The ash content was determined by igniting a dried grass sample at 700 °C and calculated as shown in equation 1.

$$\% - ash = \frac{m_{ash}}{m_{biomass}} 100 \quad (1)$$

The bulk density of sample that was sieved through 250-µm sieve was determined using a method described in the Indian Standards [9] and was calculated using equation 2.

$$\rho_{bulk} = \frac{m_{ash}}{V_{ash}} \quad (2)$$

The method for loss on ignition (LOI) was adapted from Poon et al. [10]. An elephant grass ash sample (2 g) dried at 105 °C to a constant mass was ignited at 775 °C for 1 hour. Equation 3 was used to calculate loss on ignition of the cooled sample.

$$LOI = \frac{m_1 - m_2}{m_2} 100 \quad (3)$$

The cation exchange capacity was determined in order to determine the amount of exchangeable Na, K and Mg. The method was adapted from Musyoka et al. [11]. *Pennisetum purpureum* ash (0.5 g) was stirred in 25 ml 0.1 M ammonium acetate solution of pH 2 for 1 hour. The ash was filtered off. The filtrate was filled to the 100-mm mark of a volumetric flask. The concentrations of exchangeable cations were determined using an ICP-AES instrument.

A commercially available Portland cement equivalent to ASTM Type I was used in this study. Formulations were adapted from Amudhavall and Mathew [12] and are summarized in Table 1.

Table 1: Formulations of mortar and *Pennisetum purpureum* ash

Ingredient	Control mortar	Mortar with 4:1 Cement: Ash blending ratio	Mortar with 18:7 Cement: Ash blending ratio	Mortar with 3:2 Cement: Ash blending ratio
Portland cement (g)	500	400	360	300
Graded standard sand (g)	1375	1375	1375	1375
Distilled water (ml)	242	242	242	242
<i>Pennisetum purpureum</i> ash (g)	nil	100	140	200

Compressive strength is the ability of a material to resist applied force. When the compressive strength limit is reached the material simply breaks up. Concrete cubes were cured at 27 °C over a total setting period of 28 days. Cube specimen (150 mm) of each concrete mixture were tested of their compressive strength on 2000 kN hydraulic press at a loading rate of 0.18 N/mm²/s after 3, 7 and 28 days of setting time. The compressive strength was calculated as shown in equation 4.

$$c = \frac{AL}{A} \quad (4)$$

where c is the compressive strength (kN/mm^2), AL the applied load in Newtons and A the cross sectional area in mm^2 .

A Chappelle test method adapted from Perraki et al. [13] was used to determine pozzolanic activity. To an ash sample (0.5 g) suspended in 200 ml distilled water, calcium hydroxide (1.0 g) was added. The suspension was refluxed for 16 hours. The solution was then filtered and titrated with 0.1 M HCl. A control mixture with calcium hydroxide only was also prepared. To this mixture of sugars (60 g) were added to dissolve calcium hydroxide. The pozzolanic activities were calculated as shown in equation 5.

$$mgCaO = 2 \times \frac{(V_2 - V_1)}{V_2} \times \frac{74}{56} \times 1000 \quad (5)$$

Where v_1 is the titration volume of the pozzolanic mixture (CaO and pozzolan), v_2 the titration volume of the control mixture CaO.

The method for strength activity index (SAI) was determined as reported by Papadakis et al. [14] and was calculated as shown in equation 6.

$$SAI = \frac{A}{B} \times 100 \quad (6)$$

Where A is the unconfined compressive strength of the test pozzolan specimen in MPa and B is the compressive strength of the control mortar.

A method for water absorption was adapted from Ahmadi and Shekarchi [15]. Concrete cores of 75 mm in diameter and 130 mm in height obtained from 200 mm-concrete cubes blended with pozzolan and standard brick were cured for 14 days. The cured concrete cores

were oven dried at 110°C for 72 hrs and percentage weight gain calculated

Results and Discussion

Proximate Analysis

Table 1 shows proximate analytical data and chemical composition of *Pennisetum purpureum* ashes determined using an XRF instrument. The ash content of the dried dead mass was found to be 6.3 %. This is close to what has been reported by Río et al.[16]. The elemental composition shows that the ash has a high silica content of 81.09 % which can slightly be increased by acid leaching. This is comparable with the content rice husk ashes and sugarcane bagasse ashes that have also been tested as potential pozzolanic material [17, 18]. The loss on ignition for the untreated ash and leached ash were 5.3 % and 4.04 % respectively and this may be due to unburn carbon material.

Table 2: Ash characteristics and elemental composition

	Raw ash	Acid leached ash
Grass ash content	6.3±0.001	-
Bulk density ($\text{g}\cdot\text{cm}^{-3}$)	0.27	0.27
Loss on ignition	5.3	4.04
Percentage compositions		
SiO ₂	81.09	82.92
Al ₂ O ₃	0.89	0.88
MgO	2.32	2.28
CaO	2.99	2.88
SO ₃	2.08	2.06
TiO ₂	0.05	0.05
Fe ₂ O ₃	1.85	1.64
Mn ₂ O ₃	0.09	0.08
P ₂ O ₅	1.10	1.18
Na ₂ O	0.32	0.23
K ₂ O	1.80	1.71

FTIR and Morphological Characterization

FTIR spectra of raw and acid leached *Pennisetum purpureum* ash are shown in the Figure 2. It can be concluded from intensity of typical absorption bands that the ash has high silica gel content. The strong absorption band at 1065 cm^{-1} can be attributed to asymmetric

Si-O-Si stretching vibration while the band at 960 cm^{-1} related to Si-O stretching mode. The band at 810 cm^{-1} is due to a symmetric

stretching vibration. Such IR absorption bands have been observed for silica and ash samples [19-21].

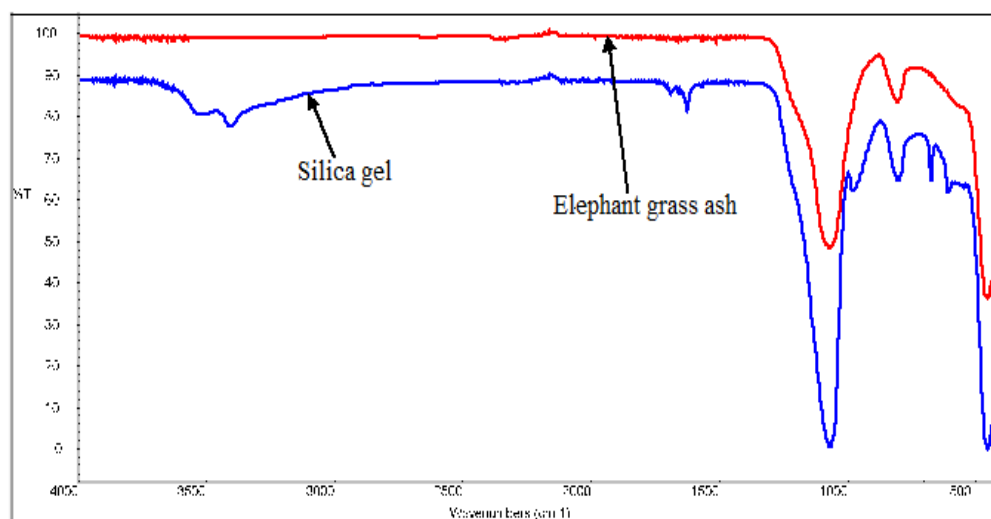


Figure 2: FTIR spectra of raw and acid leached *Pennisetum purpureum* ash

An XRD pattern for purpureum ash produced at $600\text{ }^{\circ}\text{C}$ is shown in Figure 3. It can be observed from the XRD pattern that *Pennisetum purpureum* ash is predominantly amorphous

confirmed by absence of ordered crystalline structure. The diffractogram has similarities to those reported for pure silica [22, 23].

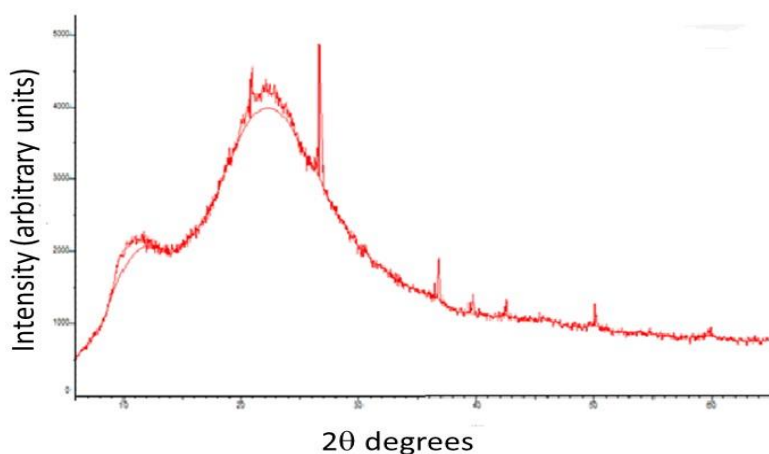


Figure 3: XRD spectrum of acid leached *Pennisetum purpureum* ash

The SEM images of *Pennisetum purpureum* ash is shown in Figure 4. The micrograph show

some evidence biomaterial despite having ignited the samples at $600\text{ }^{\circ}\text{C}$.

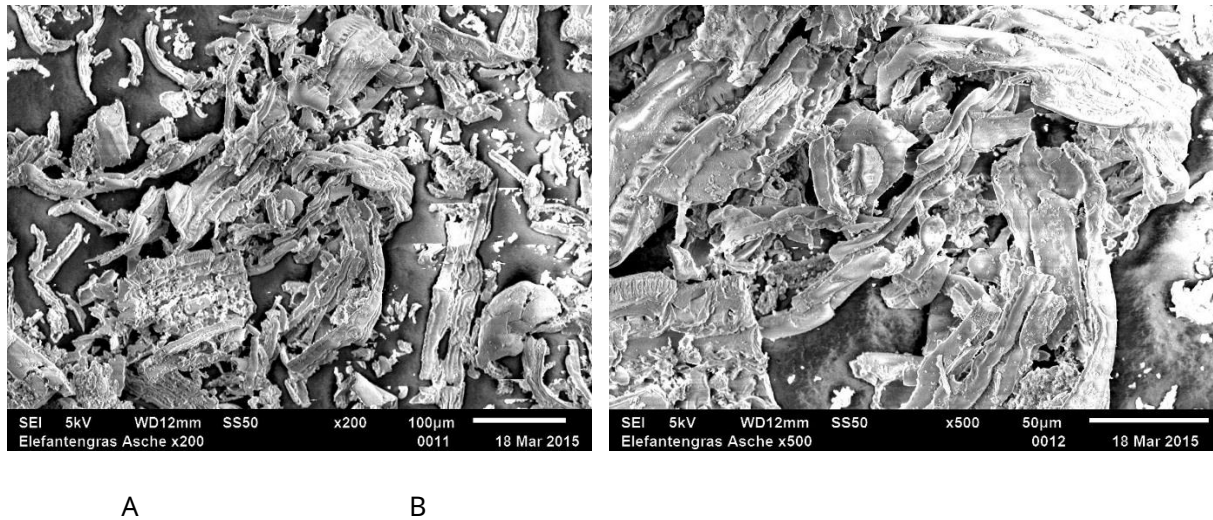


Figure 4: SEM Images of acid leached *Pennisetum purpureum* ash sample

Cation Exchange Capacities

The cation exchange capacities (CEC) of blended cement samples are shown in table 3. The results show a decrease in exchangeable Mg^{++} and Ca^{++} with increase in added pozzolan.

Table 3: Values for cation exchange capacities for blended cements in ppm

Ion type	Ash	Cement type			
		Unblended cement	With 4:1 Cement: Ash ratio	With 18:7 Cement: Ash ratio	With 3:2 Cement: Ash ratio
Na ⁺	4.60	4.60	4.50	4.60	4.68
K ⁺	4.60	12.24	19.78	12.12	11.59
Mg ⁺⁺	12.24	25.37	12.02	12.02	9.87
Ca ⁺⁺	16.60	321.00	225.01	195.01	167.07
Total	39.94	362.78	261.31	253.75	241.2

Compressive Strength

The effect of amount of pozzolan added on the compressive strength is illustrated in Figure 1 below. From the diagram it can be concluded

that compressive strength increases with increase in the percentage of the pozzolan with 4:1 blending ratios having a compressive strength comparable to the control of sample that had been aged for 28 days.

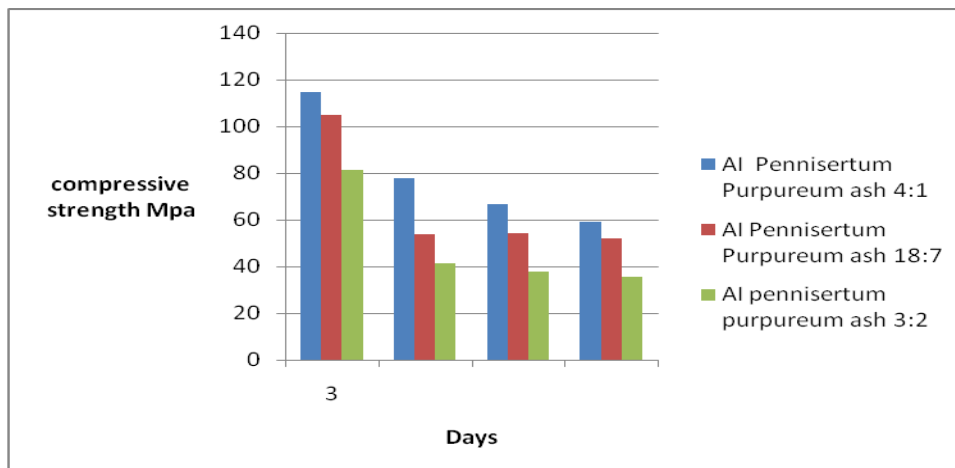


Figure 6: Effect of compressive strength on aging times

Strength activity index

The effect of the amount of pozzolan added on strength activity index is illustrated in Figure 6. From the diagram, it can be concluded that

strength activity index remained high with slight fluctuation for mortar mixtures blended with 3:2 cement: *Pennisetum purpureum* ash ratio over 28-days aging period.

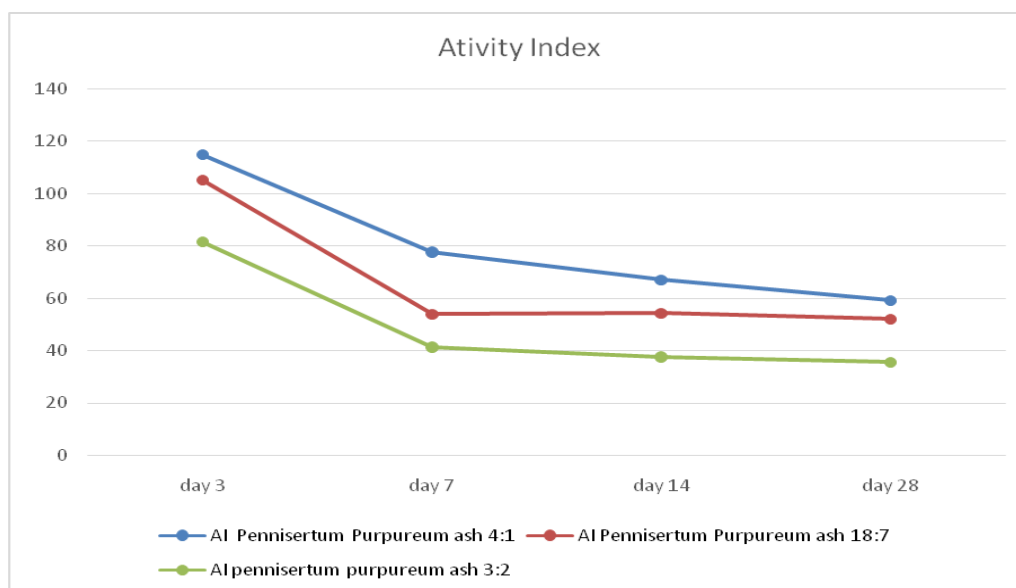


Figure 6: Effect of aging time on strength activity index

Chappelle Test

The pozzolanic reactivity of a material is measured by the amount of fixed quantity of calcium hydroxide in pozzolanic materials. This was determined by lime consumption after *Pennisetumpurpureum* ash was reacted with CaO suspended in water. The effect of lime consumption by *Pennisetum purpureum* over 28 days of setting period is illustrated in Figure 7.

From the graph it can be observed that lime consumption was high in the first 7 days of aging and increased gradually over the remainder of the period.

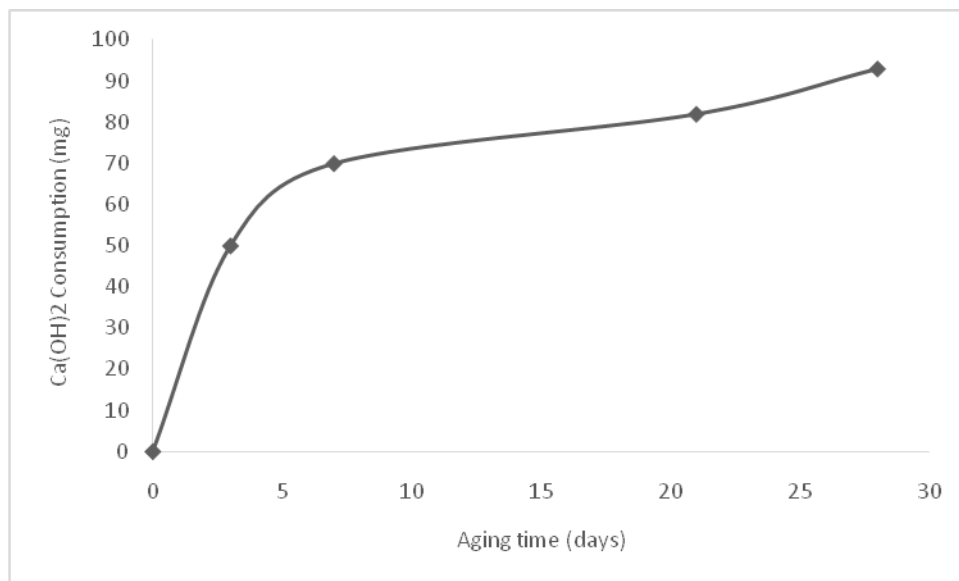


Figure 7: Lime consumption of *Pennisetum purpureum* ash

Water absorption tests

Water absorption is the weight of moisture in the pores to the weight of the mortar cubes. The effect of blending on water absorption is shown in Table 3 below. From the table it can be observed that there was a decrease in water absorption with increase in the percentage of the pozzolan.

This may be attributed to decrease in the porosity of the mortar cubes due to the small particulate nature of the added pozzolan. The average particle sizes was 26 μm and the distribution ranged from 2 μm to 100 μm (Figure 8).

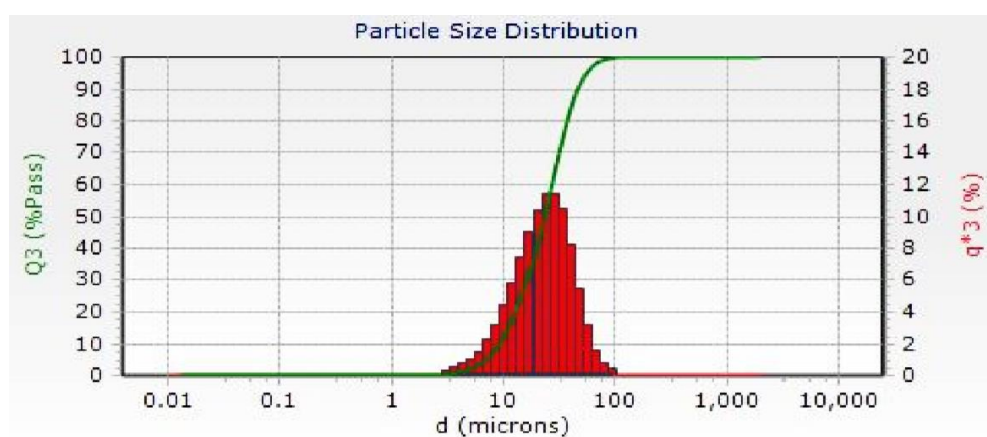


Figure 8: Particle size distribution of *Pennisetum purpureum* ash

Table 4: Effect of blending on water absorption

Type of concrete block	% water absorption
Control	2.8
4:1 Cement:Ash ratio	2.5
18:7 Cement:Ash ratio	2.1
3:2Cement:Ash ratio	2.0

Conclusion

The study showed that *Pennisetum purpureum* grass ash has good pozzolanic properties and hence can be used as a cement replacement. Portland cement with a blending ratio of 3:2 showed good binding properties comparable to Portland cement Type I. Cement mortar with lower replacements tended to age slowly and failed to reach the compressive strength of the control in 28 days of aging. Given the abundant nature of elephant grass, it can be concluded that elephant grass ash is a viable renewable pozzolanic material.

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References

- Huntzinger, D.N., Eaton, T.D. (2009). A life-cycle assessment of Portland cement manufacturing: Comparing the traditional process with alternative technologies. *Journal of Cleaner Production*, 17, 668-675.
- Worrell, R., Orice, I., Martin, N., Hendriks, C., and Meida, L. O. (2001). Carbon dioxide emissions from the global cement industry, *Ann. Rev. Energy Environ*, 26, 303-329.
- Habeeb, G.A. and Fayyadh, M.M., (2009). Rice Husk Ash concrete: The effect of RHA average particle size on mechanical properties and drying and shrinkage. *Australian Journal of Basic and Applied Sciences* 3(3) 1617-1622.
- Salas, A., Delvasto, S., Gutierrez, M.R., and Lange, D. (2009). Comparison of two processes for treating rice husk ash for used in high performance concrete. *Concrete and Concrete Research* 39, 773-778.
- Madandoust, R., Sobhani, J., and Ashoori, P. (2013). Concrete made with zeolite and metakaolin: A comparison on the strength and durability properties. *Asian Journal of Civil Engineering* 14(4), 533-543.
- Courard, L., Darimont, A., Schouterden, M., Ferauche, F., Willem, X., and Degeimbre, R. (2003). Durability of mortars modified with metakaolin. *Cement & Concrete Research* 33, 1473-1479.
- Wong, H.S., and Razak, H.A. (2005). Efficiency of calcined kaolin and silica fume as a cement replacement material for strength performance. *Cement & Concrete Research* 35, 696-702.
- Kiattikomol, K., Jaturapitakkul, C., Songpiriyakij, S., and Chutubin, S. (2001). A study of ground coarse fly ashes with different fineness from various sources as pozzolanic materials. *Cement & Concrete* 23, 335-343.
- IS:1727: (1967). *Indian Standard-Methods of test for Pozzolanic Materials*. Indian Standards Institute, Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 1, India.
- Poon, C.S., Lam, L., and Wong, Y.L., (1999). Effects of fly ash and silica fume on interfacial porosity and chloride diffusivity of concrete. *Journal of Materials in Civil Engineering*, 427-432.
- Musyoka, N.M., Petrik, L.F., Balfour, G., Misheer, N., Gitari, W., and Mabovu, B. (2009). *Removal of toxic elements from brine using zeolite Na-PI from South African Coal Fly ash, Conference Proceedings*. International Mine Water Conference 9-23 October, 2009.
- Amudhavall, N.K., and Mathew, J. (2012) Effect of silica fume on strength and durability parameters of concrete. *International Journal of Engineering Sciences & Emerging Technologies* 3(1), 28-35.
- Perraki, T., Kentori, E., and Tsivilis, G. (2012). The effect of zeolite on the properties and hydration of blended cements, *Concrete and Concrete Composites* 32(2), 14-37.
- Papadakis, V.G., Antiohos, S., and Tsimas, S. (2002). Supplementary cementing materials in concrete Part II: A fundamental estimation

- of the efficiency factor, *Cement & Concrete Research* 32, 1533-1538.
- Ahmadi, B., and Shekarchi, M. (2010). Use of natural zeolites as supplementary cementitious material, *Concrete & Concrete Composites* 32 134-141.
- Río, J.C., Prinsen, P., Rencoret, J., Nieto, L., Jiménez-Barbero, J., Ralph, J., Martínez, A.T., and Gutiérrez, (2012). A. Structural characterization of the lignin in the cortex and pith of the elephant grass (*Pennisetum purpureum*) stem. *Journal of Agricultural and Food Chemistry* 60, 3619-3634, [dx.doi.org/10.1021/jf300099g](https://doi.org/10.1021/jf300099g).
- Ugheoke, I.B., and Mamat, O.A. (2012). A critical assessment and new research directions of rice husk silica processing methods and properties. Maejo International Journal of Science and Technology 6(3) 430-448.
- Teixeira, S.R. (2010). Crystallization of SiO₂-CaO-Na₂O glass using sugarcane bagasse ash as a silica source. *Journal of the American Ceramic Society* 93(2) 450-455. DOI:10.1111/j.1551-2916.03431.x.
- Essien, E.R., Olaniyi, O.A., Adams, L.A. and Shaibu, R.O. (2012). Sol-gel derived porous silica: Economic synthesis and characterization. *Journal of Minerals and Materials Characterization and Engineering* 11 976-981.
- Singh, L.P., Agarwal, L.P., Bhattacharyya, S.K., Sharma, U., and Ahalawat, S. (2012). Preparation of silica nanoparticles and its beneficial role in cementitious materials, *Nanomater. Nanotechnol.* 1(1), 44-51.
- Nayak, J.P. and Bera, J. (2009) Preparation of silica aerogel by ambient pressure drying process using rice husk ash as raw material, *Trans. Ind. Ceram. Soc.* 68(2), 1-4.
- Adam, T., and Chew, S. (2011). A simple template-free sol-gel synthesis of spherical nanosilica from agricultural biomass. *J. Sol-Gel Sci. Technol.* 59, 580-583. Doi: 10.1007/s10971-011-2531-7.
- Essien, E.R., Olaniyi, O.A., Adams, L.A., and Shaibu, R.O. (2011). Highly porous silica network prepared from sodium metasilicate, *Journal of Metals, Materials and Minerals* 21(2) 7-12.
- United Nations (1989). *The United Nations Convention on the Rights of a Child. Unpublished report*, Geneva.